

Catalytic Oxidation of Volatile Organic Compounds by Using Spinel Mixed Oxide Catalyst- A Review

Seyed Ali Hosseini

Department of Applied Chemistry, Faculty of Chemistry, Urmia University, Urmia, Iran
s_ali_hosseini@yahoo.com. a.hosseini@urmia.ac.ir

Abstract

Volatile organic compounds (VOCs) are the main sources of air pollution because of their toxic properties. Recently, catalytic combustion presents many advantages, such as high combustion efficiency and low emission of unburnt hydrocarbons. Among some techniques used to reduce VOC emission, catalytic oxidation is recommended especially for highly diluted VOCs. Selection of catalytic materials for the reduction of VOCs is not easy because the activity depends on the specific molecule, synthesis method and many parameters can affect the catalyst activity and resistance. Spinel type mixed metal oxides are considered as novel catalysts for remediation of volatile organic compounds promising because of their catalytic activity and robust stability. The present review focuses on the application of spinel type mixed oxides in combustion of VOCs. The effects of synthesis method, promoter and particle size dependence are discussed. The proposed reaction mechanism for combustion of VOCs over these catalysts is addressed.

Keywords

Spinel; Mixed Oxide; Ceramics; Catalytic Combustion; Volatile Organic Compounds

Introduction

Volatile organic compounds have a high vapor pressure and low water solubility.

Volatile organic compounds (VOCs) include most solvent thinners, degreasers, cleaners, lubricants, and liquid fuels [1]. These compounds are the common air pollutants emitted by the automobiles, chemical and petrochemical industries. Emissions of VOCs originate from breathing and loading losses from storage tanks, venting of process vessels, leaks from piping and equipment, wastewater streams and heat exchange systems. A brief list of some common VOCs are presented in table 1[2]. As it is observed, various groups of organic compounds such as methane, ethane, tetrachloroethane, methyl chloride, and various chloro hydrocarbons and perfluoro carbons are included [2].

VOCs in gaseous streams are potential air pollutants due to their malodorous and hazardous properties. Eye and throat irritation, damage to liver, central nervous system, all may occur due to the prolonged exposure to VOCs. VOCs may also have carcinogenic effects [3]. Studies on carcinogenicity of certain classes of hydrocarbons indicate that some cancers appear to be caused by exposure to aromatic hydrocarbons found in soot and tars. In addition, VOCs can contribute to global warming, stratospheric ozone depletion and tropospheric ozone formation. VOCs may undergo photochemical reactions with nitrogen oxides in the presence of sunlight, yielding even more hazardous compounds, such as troposphere ozone or organic peroxides (the so-called photochemical smog) [1].

For this reason, VOCs are being subject to increasingly severe constrains; in Europe, for example, VOCs are controlled through the EU Directive 1999/13/EC on the limitation of emissions of volatile organic compounds [4].

Control of VOCs emission is a major concern of the industries' commitment towards the environment. Regulations on controlling organic vapor pollutants in air have been issued world-wide. In the ambient air quality standards produced by the US Environmental Protection Agency, the maximum 3-hour concentration of hydrocarbon content is 1.6×10^{-4} kg/m³ (0.24 ppm), not to be exceeded for more than a year [2].

TABLE 1. SOME OF COMMON VOCs [2]

	Type of VOCs	Example
1	Aldehyde	Formaldehyde, Acetaldehyde
2	Chloro hydrocarbons	Methyl chloride, Carbon tetrachloride
3	Esters	Ethyl acetate
4	Alcohols	Isopropyl alcohol, 1 Ethylene glycol
5	Alkanes	Hexane, heptane
6	Ketone	Acetone, Methyl ethyl ketone
7	Ethers	Mono methyl ether
8	Aromatics	Benzene, toluene, Xylene, Styrene, Naphthalene

There are many different techniques available to control VOCs emissions. These techniques are basically classified into two different groups: (i) process and equipment modification and (ii) add-on-control techniques. In the first group, control of VOCs emissions is achieved by modifying the process equipment, raw material, and/or change of process, while in the other class an additional control method has to be adopted to regulate emissions. Though the former is the most effective and efficient method, its applicability is limited, as usually it is not possible to modify the process and/or the equipment. The techniques of second group are divided into subsection i.e. recovery and destruction techniques. The techniques of recovery include: membrane separation, condensation, adsorption and absorption, whereas the destruction techniques include oxidation and bio-filtration techniques. Selection between different alternatives depends on the nature, flow rate, concentration of pollutants, outlet required concentration, and other circumstances such as presence of solids or poisons for catalysts. Since the concentration of volatile organic compounds in air is very low, the destruction techniques especially oxidation methods are used [5].

Thermal oxidation systems combust the organic compounds at 1300–1800 °F. Actual operating temperature is a function of the type and concentration of material in the vent stream and the desired destruction and removal efficiency. Catalytic oxidation systems directly combust VOCs in a manner similar to thermal oxidizers. The main difference is that the catalytic system operates at a lower temperature-typically about 700–900°F. Thermal combustion is the most extended method for abatement of VOCs, but it is not a feasible process as it operates at a high temperature, usually above 1273 K. It requires additional fuel and the use of temperature-resistant materials, and it generates noxious byproducts (NO_x). Catalytic combustion appears to be the most promising solution for elimination of VOCs when they are at low concentrations. Catalytic combustion offers environmental advantages, since it operates at much lower temperatures, avoiding formation of nitrogen oxides [6]. Heterogeneous catalytic oxidation is a well-studied and industrially useful process. The catalyst and its physicochemical properties have a main influence on efficiency of catalytic oxidation process. Noble metals and transition metal supported are two types of catalysts used in catalytic oxidation processes. Although the noble metal catalysts successfully degrade volatile organic compounds, they are not adopted to large-scale applications owing to their high cost and rapid deactivation because of sulfur and chlorine poisoning. Recently a review paper has been published by Liotta about catalytic oxidation of volatile organic compounds on supported noble metals [7]. He reviewed the papers on the most used noble metals catalysts for oxidation of not halogenated VOC. The effects of metal salt precursor, chlorine poisoning, water inhibition, particle size dependence, nature of the support were discussed. The calculated reaction order with respect to VOC and oxygen as well as the proposed reaction mechanisms were addressed.

Driven by the need for decreasing manufacturing cost and increasing resistance to poisoning of commercial catalysts for volatile organic compounds (VOCs) elimination, efforts have been made to develop metal oxide catalysts, which can exhibit activity similar or higher than of noble metal catalysts. Therefore, many efforts have been made to find the transition metal oxide catalysts or partially replace the noble metal catalysts, which can exhibit similar or higher activity than that of the noble metal catalysts [8-10]. They are commonly deposited on suitable supports. These catalysts are extensively used for catalytic combustion of volatile organic compounds. Most of used catalysts are single or bi-metals without formation of special structure, which are supported on high surface area supports [11-14].

Consequently, conventional catalytic oxidation usually requires temperatures above 200°C. Therefore, the synthesis of a new material for the catalytic combustion of hydrocarbons at lower temperatures would be

significant. The used catalysts are single or bi-metals which are supported over supports. The need to develop the new catalyst causes the development of new type of catalysts. Mixed oxides because of having some advantages are more promising [15].

The paper would give an overview of spinel type mixed oxides in catalytic oxidation of volatile organic compounds.

Catalysts Used for VOC Remediation

Complex oxides (containing two or more types of cations) with spinel structure are of intense interests in the material research because of their remarkable optical, electrical, magnetic catalytic properties and applications in science and engineering [16]. A typical ordered spinel is a ternary chemical compound of general formula of AB_2O_4 . It has two cations, a cation with an oxidation state of 2+, and B, 3+. The core of the spinel structure is a face-centered cube with all of its corners occupied by oxygen atoms. Assuming that the crystal structure consists of polyhedral, two kinds of voids can be readily discerned inside the cube, which might be assigned the shape of an octahedron and a tetrahedron, respectively [17]. Due to their remarkable catalytic properties including high melting points and high surface areas, the metal oxide composites with spinel structure are increasingly being investigated as catalysts for the treatment of environmental pollutants. Among them Co, Cu, Cr, and Mn oxides are the most frequently used for total oxidation of hydrocarbons [18-19]. Many parameters could influence on the activity of spinel type catalysts. One of factors which influences on the activity of catalyst is the preparation method. The primary goal of the preparation is an optimizing of the synthesis conditions to obtain oxide catalysts with desired crystal structure as well as high specific surface area. Different methods are used for preparation of spinel oxides. The most common methods are sol gel combustion, co-precipitation, and pechini type sol gel, and layered double hydroxide. Herein we present some papers in which spinels catalysts, prepared by different methods, have been used in catalytic combustion of VOCs.

U. Zavyalova et al. [20] reported the elimination of n-hexane over spinel structure AB_2O_4 (where A = Co, Cu and B = Cr, Co) synthesized by sol gel combustion method. They used from different precursors to synthesize of spinels. There is a clear difference between the catalytic performances of the mixed oxides prepared by GCS from various fuels. The fig.1 shows that the samples synthesized from glycerin/nitrate mixtures were more active compared with the catalysts prepared from glycine/nitrate. It is noteworthy that the interaction of glycerin with metal nitrate in solution is a complex process accompanied with the formation of glycerin associates over a wide range of temperatures and viscosities. The order for activity of catalysts was as follows: $CuCo_2O_4 > Co_3O_4 > CoCr_2O_4$. They concluded that catalytic performance of the GCS catalysts in the VOCs (n-hexane) elimination correlates with structural and textural properties of the Co-based spinels, which in turns are influenced by the preparation and precursor used. The best catalytic performance in hexane elimination was obtained over copper cobaltite catalyst prepared by combustion of glycerin chelated metal nitrates.

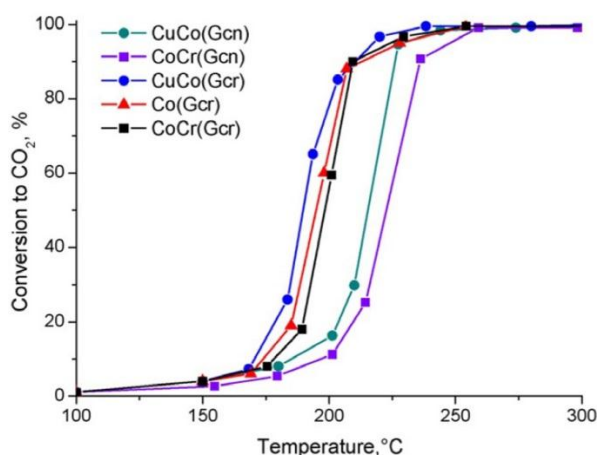


FIG.1. LIGHT-OFF CURVES FOR THE CONVERSION OF N-HEXANE OVER SPINELS [20]

Flavia G. Dura' et al. used manganese and iron mixed oxides, synthesized by sol gel combustion as combustion catalysts of ethanol, ethyl acetate and toluene and concluded that the total combustion of on these samples over

mixed oxides were better than on Fe_2O_3 and Mn_2O_3 pure oxides [21].

Fino and co-workers [22] prepared the four spinel-type catalysts AB_2O_4 (CoCr_2O_4 , MnCr_2O_4 , MgFe_2O_4 and CoFe_2O_4) and studied the activity of these catalysts towards the combustion of methane in a temperature-programmed combustion (TPC) apparatus. The samples were synthesized by solution combustion synthesis (SCS) using urea as fuel. Spinel-type-oxides containing Cr at the B site were found to provide the best results. The half-conversion temperature of methane over the CoCr_2O_4 catalyst was 376 °C with a $W/F = 0.12 \text{ g s/cm}^3$. They studied the catalysts using TPD. On the basis of temperature-programmed oxygen desorption (TPD) analysis as well as of catalytic combustion runs, the prevalent activity of the CoCr_2O_4 catalyst was explained by its higher capability to deliver superficial, weakly chemisorbed oxygen species. This catalyst, promoted by the presence of 1 wt% of palladium deposited by wet impregnation, was lined on cordierite monoliths and then tested in a lab-scale test rig. The combination of Pd and CoCr_2O_4 catalysts enables half methane conversion at 330 °C ($\text{GHSV} = 10,000 \text{ h}^{-1}$), a performance similar to that of conventional 4 wt% Pd- $\gamma\text{-Al}_2\text{O}_3$ catalysts but enabled with just a four-fold lower amount of noble metal.

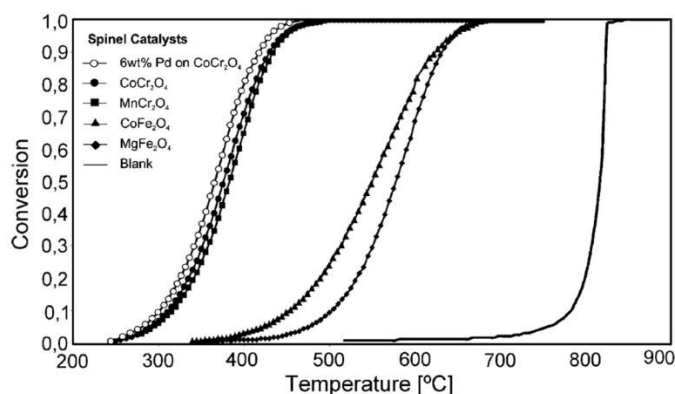


FIG.2. LIGHT-OFF CURVES FOR COMBUSTION OF METHANE OVER SPINEL CATALYSTS

Spasova et al [23] reported the complete oxidation of methyl ethyl ketone and toluene over Cu-Cr and Co-Cr supported on alumina and silica-alumina. They concluded that the activity was determined by the spinel phase formation and the presence of couples of transition metal ions in different oxidation states.

Kim and Ihm [24] used various chromium-containing catalysts prepared by co-precipitation methods for the total oxidation of trichloroethylene (TCE) as a model reaction for the catalytic combustion of chlorinated organic pollutants. Cobalt chromite (CoCr_2O_4) of spinel-type was proven to be a very promising catalyst showing higher activity and higher CO_2 selectivity than traditional alumina supported chromia catalysts.

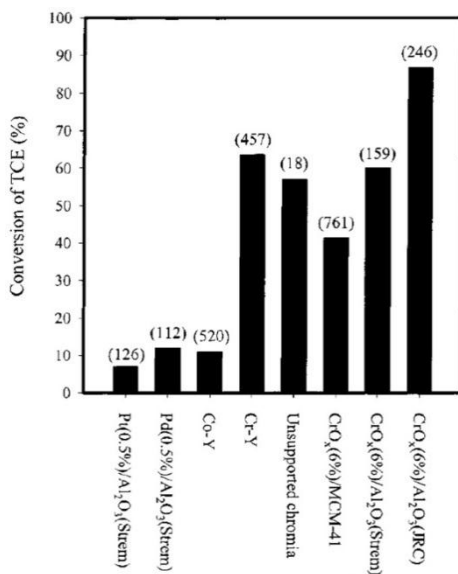


FIG.3. CATALYTIC ACTIVITY FOR THE DECOMPOSITION OF TCE AT 350 °C OVER VARIOUS CATALYSTS. THE NUMBERS IN PARENTHESES ARE SURFACE AREAS (M^2/G) [24].

They concluded that the Cr^{6+} species is very stable under reducing environment. The presence of Cr^{3+} - Cr^{6+} pair sites and the effect of redox treatments on the activity were investigated to explain the nature of possible active sites for TCE decomposition. Higher selectivity to CO_2 of CoCr_2O_4 was ascribed to the abundance of its Cr^{3+} species, together with its activity for water gas shift reaction. Sometimes, supported transition metal oxides show better activity than supported noble metal catalysts in combustion of VOCs. Fig.3 summarizes the results of reaction experiments with various catalysts for decomposition of TCE at 350 °C. Supported noble metals such as Pt or Pd were not effective for the TCE decomposition mostly due to their rapid deactivation even during the first 1-h of reaction, also as reported by Marceau et al. [25] for the alumina-supported Pt catalysts. While Cr-Y was very active for the TCE decomposition, Co-Y was inactive.

Fan et al. prepared a series of catalyst candidates based on aluminum spinels and iron spinels, XAl_2O_4 and XFe_2O_4 (X: Mg, Ca, Cu, Ni, Zn), were prepared by co-precipitation at pH=8 and calcination at different temperatures [26].

Destruction of polychlorinated aromatic compounds was carried out over spinel-type catalysts.

Fig.4 shows the catalytic activities of Mg-Al and Mg-Fe spinels formed at different calcination temperatures were evaluated by the degradation of hexachlorobenzene (HCB) at the reaction temperature of 250 and 300 °C, respectively. The MgAl_{600} showed the highest dechlorination efficiency among the Mg-Al spinels both at 250 and 300 °C. The Mg-Fe spinels calcined at different temperatures also showed different hydrodechlorination activities. However, Mg-Fe_{400} and Mg-Fe_{300} had the highest dechlorination efficiency at 250 and 300 °C, respectively. The average degree of chlorination for chlorobenzenes (average number of chlorine substituents) after thermal treatment of HCB was 3.0 for MgAl_{600} and 2.0 for MgFe_{600} at 300 °C. The tendency of dechlorination efficiency with calcination temperature varied with the chemical compositions of spinel. On the other hand, since the chemical compositions of Mg-Al/Mg-Fe spinels were similar, the difference in the activity was possibly related to the structure of samples. Among all studied spinels, the copper-aluminum spinel (CuAl_2O_4), specifically calcined at 600 °C, and exhibited the best activity (Fig.5). The complete conversion of organic compounds over this catalyst was concluded at 350°C.

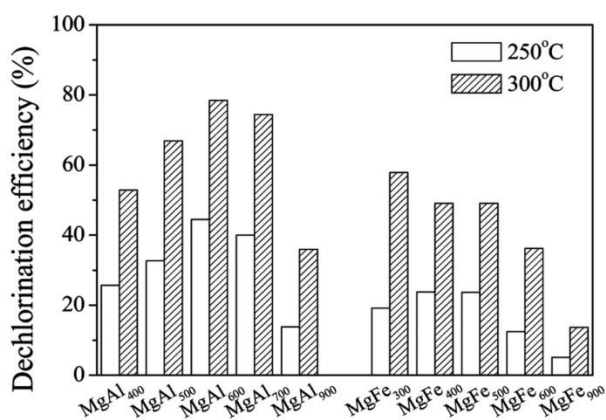


FIG.4. DECHLORINATION EFFICIENCY OF HCB ON DIFFERENT SPINEL-TYPE CATALYSTS (REACTION TIME: 30 MIN; CATALYST DOSE: 100 MG [26].

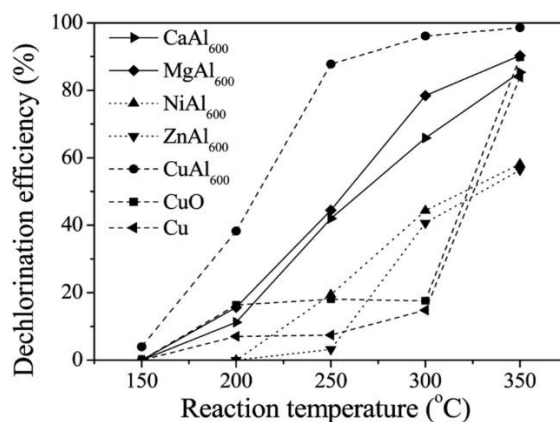


FIG.5. COMPARISON OF DECHLORINATION EFFICIENCY OF HCB ON ALUMINUM-BASED SPINELS, CU AND CUO (REACTION TIME: 30 MIN; CATALYST DOSE: 100 MG) [26]

Baldi et al. [27] have reported the application of mixed manganese and ferrous oxides in catalytic combustion of VOCs. They prepared Mn_2O_3 - Fe_2O_3 mixtures by co-precipitation of manganese acetate and iron nitrate in ammonium carbonate aqueous solution. After the ageing, the precipitated fraction was filtered, dried and calcined at 1073 K for 3 h. They showed that these materials are active catalysts for the catalytic oxidation of propane and propene at low temperatures. They proposed synergy between iron and manganese oxide components. The phase diagram for Mn-Fe-O system has been published by Kedesdy and Tauber [28]. The formation of several arrangements such as solid solution or $\text{Fe}_x\text{Mn}_y\text{O}_4$ spinels has been proposed. It has also been observed that transition metals such as Mn, in the spinel lattice can strongly modify the redox properties of the ferrites and thus influence on their stability. Another method which has been reported for spinel catalyst preparation for VOC oxidation is layered double hydroxide (LDH).

František Kovanda et al. [29] studied the application of mixed oxides catalysts for total oxidation of volatile organic compounds. Structured mixed oxide catalysts were prepared by the calcination of layered double hydroxides

(LDHs) deposited on $\text{Al}_2\text{O}_3/\text{Al}$ supports (anodized aluminum foil). The deposition of LDH precursors on the supports was carried out under hydrothermal conditions at 140 °C in aqueous solutions of Ni, Co, Cu, and Mn nitrates. MII-(Mn)-Al LDHs (MII = Ni, Co, Ni-Co, Ni-Cu, and Co-Cu) with only slight Mn contents were obtained. An increased pH of the solutions used for deposition enhanced the formation of LDH phases. After heating at 500 °C, spinel-like and/or NiO-like oxides were detected in the supported mixed oxides. Compared with the mixed oxides obtained by calcination of the co-precipitated LDH precursors, the supported mixed oxides exhibited worse reducibility and lower catalytic activity in the total oxidation of ethanol; both the formation of spinel-like phases and high structural ordering of the products deposited on the $\text{Al}_2\text{O}_3/\text{Al}$ supports could explain the poor reducibility. Among the supported catalysts, the Ni-Cu-(Mn)-Al mixed oxide was the most active in the total oxidation of ethanol. Increasing the pH of solutions used during the hydrothermal deposition of the LDH precursors resulted in improved catalytic activity and selectivity of the supported mixed oxides. Cobalt is an active metal in catalytic combustion of hydrocarbons. It could form a spinel structure, Co_3O_4 , which exhibits good activity for oxidation of VOCs. Rivas et al. [30] reported the synthesis and characterization of several nanocrystalline Co_3O_4 catalysts and study of their activity and selectivity during the oxidation of 1, 2-dichloroethane, as a model chlorinated volatile organic compound. A wide number of synthesis routes starting from cobalt (II) nitrate were examined, namely calcination of the precursor salt, solid-state reaction, precipitation and sol-gel. Fig.6 shows the structure of catalysts. All samples show the spinel structure with different intensity. The catalysts prepared by precipitation decomposed the chlorinated feed at the lowest temperatures (Fig.7). Activity was observed to be chiefly governed by a small crystallite size which may give rise to more easily accessible active sites (oxygen $-\text{O}^\cdot$ or O^{2-} species), which were not present on the more highly crystalline Co_3O_4 catalysts. Interestingly, the behaviour of some of the nanocrystalline oxides was superior to that of supported noble metal catalysts and other bulk oxide catalysts. Conversion to deep oxidation products was complete (CO_2 , HCl and Cl_2), and no appreciable deactivation with time on stream was noticed.

The samples calcined at 500 °C were first examined, since it was a priori expected that the oxidation process under the tested experimental conditions would require relatively high reaction temperatures due to the known stability of chlorinated VOCs. The results from the homogeneous reaction (the catalyst was replaced by inert quartz particles) are also included for comparative purposes. DCE conversion in the absence of any catalyst did not start prior to 350 °C and reached only 20% conversion at 500 °C. In contrast, the use of Co_3O_4 oxide as catalyst significantly accelerated the desired reaction, and in all cases the chlorinated compound was completely abated between 325 and 500 °C, which compared very favourably with temperatures in excess of 500 °C, which would be required for thermal combustion. Nevertheless, substantial differences were clearly evident depending on the used synthesis route, thus revealing that the preparation method would be a key factor for obtaining a highly active Co_3O_4 catalyst. Hence, the range at which the 50% conversion was achieved varied between 250 and 380 °C, whereas the temperature for complete removal (90% conversion) was in the 325–500 °C range.

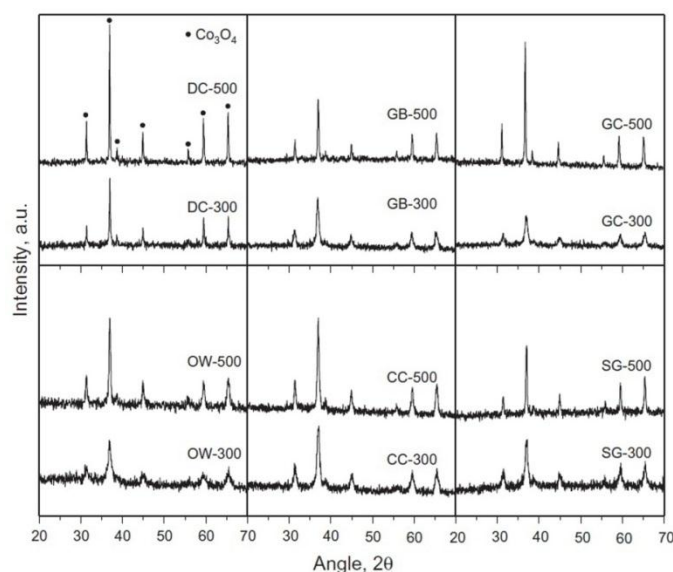


FIG.6. XRD PATTERN OF Co_3O_4 OBTAINED BY DIFFERENT METHODS [30]

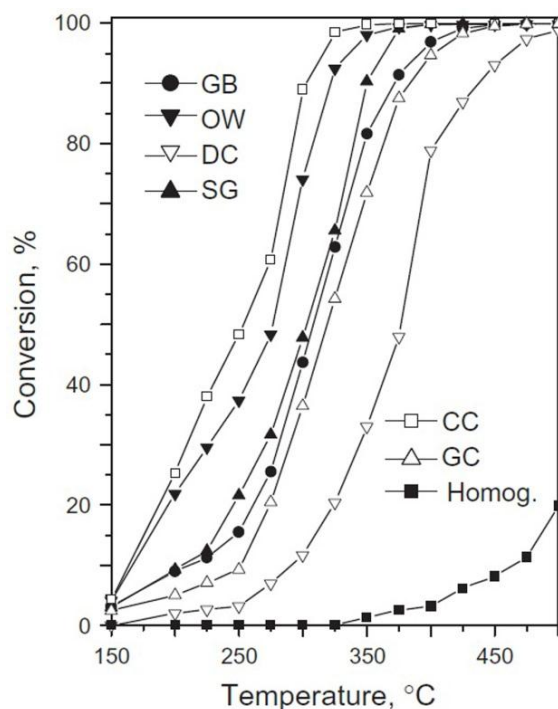
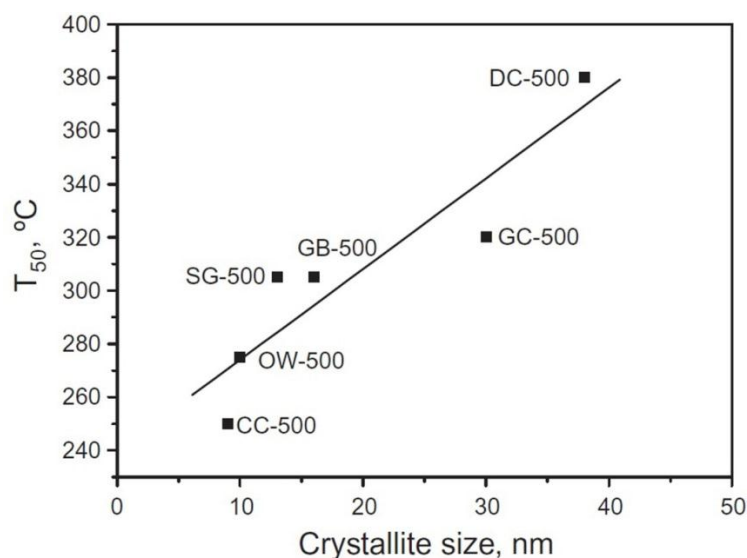


FIG.7. LIGHT OFF CURVES FOR CONVERSION OF DCE OVER CATALYSTS [30]

Although all the cobalt oxide catalysts were comprised of the same phase, Co_3O_4 , Fig. 8 suggests that a certain dependence of activity on crystallite size exists, which in turn is very closely related to the redox properties of the samples. As a general behaviour, a lower crystallite size decreased the temperature for DCE 50% conversion. On the basis of the assumption, the reaction occurs through a Mars–Van Krevelen mechanism involving lattice oxygen via a redox cycle [31, 32, 33].

FIG.8. THE RELATIONSHIP BETWEEN ACTIVITY OF CATALYST AND CRYSTAL SIZE OF Co_3O_4 [30]

Another parameter that changes the activity of spinel catalyst is to use promoter materials.

A new and simple method for obtaining highly dispersed Co/ZrO_2 catalyst was described by Wyrwalski and his co-worker. They studied the effect of ethylenediamine on activity of Co/ZrO_2 [34]. They studied the presence of ethylenediamine during the preparation of Co/ZrO_2 and compared with a reference catalyst conventionally prepared. They found that the addition of an aqueous solution of ethylene diamine to a cobalt nitrate solution had a dramatic effect on the catalytic performance of the catalyst as compared with a reference catalyst. This promotional effect was explained in terms of higher cobalt dispersion in the catalysts using ethylene diamine. The reason why ethylenediamine improves dispersion of the cobalt species was explained in terms of the size of the

stable complex ions which could be formed in situ during impregnation. The best catalytic results were also explained in terms of Co-support interaction since new cobalt species were reducible at lower temperatures.

Chen and Zheng reported the effect of K and Al over NiCo_2O_4 catalyst on its character and catalytic oxidation of VOCs. The properties of these three samples were investigated by X-ray powder diffraction (XRD), temperature-programmed reduction (TPR), Brunauer–Emmett–Teller (BET) measurement, and X-ray photoelectron spectroscopy (XPS) technologies. The catalytic activity of volatile organic compounds (VOCs) oxidation was found to be decreased after adding aluminum and increased after adding potassium in NiCo_2O_4 sample. The small particle size of NiCo_2O_4 was responsible for VOCs oxidation. The potassium was the most effective in promoting NiCo_2O_4 sample in reducibility and surface area. XPS analysis indicated that the electrophonic oxygen species on the catalyst surface is the main active oxygen and plays an important role in total oxidation of VOCs.

Application of ultrasound waves in preparation of nanocatalysts has been reported, which could change the activity of catalyst. For example, the effect of ultrasound in synthesis in the synthesis of catalysts of cobalt oxides prepared starting from the coprecipitation method of a hydrotalcite structure was investigated by Pérez and co-workers [36]. They characterized the samples by XRD, XRF, BET, TPR and TPO. The characterizations confirmed the success of the synthesis of hydrotalcites as precursors of mixed oxides using ultrasound as an aging method, if given the same structural properties. The hydrotalcites used as precursors for the obtaining of mixed solids are excellent catalysts in the oxidation reactions of VOCs with high selectivity towards products of total combustion, showing that ultrasound is an effective and novel technique to get solids with better catalytic properties.

The oxidation of organic molecules over metal oxides usually proceeds according to the Mars and van Krevelen (MVK) mechanism, where the organic molecule is oxidized by the lattice oxygen of the oxide, the latter being re-oxidized by gas phase oxygen [37]. Therefore, the availability and reactivity of surface oxygen species provide a method for the identification of the most active catalyst. Therefore, in the case of mixed metal oxides the activity is determined by the lattice oxygen, the nature of metal, specific surface area and etc. The synthesis method of spinel catalyst affects the above factors [38-43].

Conclusion

From the present review, it is concluded that spinel structure spinel type metal oxides are promising catalysts for remediation of volatile organic compounds. They exhibit high activity and robust stability for combustion of volatile organic compounds. The synthesis method, calcinations temperature, precursors and promoters affect the activity and physic-chemical properties of spinel catalysts. Spinels with smaller particle sizes often show higher activity because of higher specific surface area and also superficial chemisorbed oxygen. Consequently, it is proposed that future research should be focused on the development of new synthesis routes leading to thermally stable samples with an even lower crystallite size (<10 nm). It is suggested that combination of noble metals and spinel type mixed oxides could be promising for combustion of environmental control.

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